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(54) Refrigeration lubricants.

(57) A lubricant comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of trimethylol ethane, trimethylol propane and trimethylol butane with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18. This lubricant is used for compressors using a hydrofluorocarbon refrigerant containing no chlorine.

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This inv ntion relates to lubricants used with r frigerants, and mor particularly to lubricants suitable for use in th compr ssion of r frigerants containing no chlorine such as hydroflorocarbons (HFC), pr ferably HFC-134a (1,1,1,2-t trafluoroethan) and th lik .

Heretofore, compounds containing fluorine and chlorin as a constitu nt l m nt such as R-11 (trichloromonofluoromethane), R-12 (dichlorodifluoromethane) as a chlorofluorocarbon (CFC), R-22 (monochlorodifluoromethane) as a hydrochlorofluorocarbon (HCFC) and the like have been used as a refrigerant for freezers, air conditioners, refrigerators and the like. In connection with recent problem on breakage of ozone layer, new refrigerants containing no chlorine such as HFC-134a and so on are proposed as a possible replacement for R-12, causing no breakage of ozone layer.

As a refrigeration lubricant, there are known many mineral-series and synthetic oils. However, it has been confirmed that these oils are very poor in the compatibility with HFC-134a and can not be applied thereto. Therefore, it is important to take a countermeasure on this problem at the present. Furthermore, the lubricity, electric insulating property, energy saving property, anti-wear performance, sealability, thermal stability, prevention of sludge formation and the like are mentioned as performances required in the refrigeration lubricant, so that they are required to be considered in the development of the above countermeasure.

Incidentally, there have hitherto been known polyether series synthetic lubricants as a synthetic oil, which are reported in Journal of the Oil Chemistry, vol. 29, No. 9, pp 336-343 (1980) and Journal of the Petroleum Technology, vol. 8, No. 6, pp 562-566 (1985). Furthermore, Japanese Patent laid open No. 61-281199 describes a mixture of polyglycol represented by a general formula of $R_1[O-(R_2O)_m-R_3]_n$, an alkylbenzene and the like, and Japanese Patent laid open No. 57-63395 describes an oil obtained by mixing a polyether such as high molecular weight polyoxypropylene monobutyl ether with an epoxycycloalkyl compound, and Japanese Patent laid open No. 59-117590 describes a high viscosity mixed oil of a polyether compound and a paraffinic or naphthanic mineral oil.

However, the conventional synthetic lubricants as mentioned above can not be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of compatibility and the like.

In US Patent No. 4,755,316, polyoxyalkylene glycol (hereinafter abbreviated as PAG) having hydroxyl groups (-OH) at both terminals is reported as a refrigeration lubricant using HFC-134a. Further, it is described that PAG is dissolved in HFC-134a within a wide temperature range as compared with general PAG containing hydroxyl group and alkyl group at its terminals, whereby the recycle of the lubricant into a compressor is improved in the refrigeration system and the seizuring in the actuation of the compressor at high temperature is prevented. Moreover, the temperature range compatible with HFC-134a is described to be between -40°C and +50°C.

On the contrary, HFC-134a is a replacing refrigerant of R-12 and is mainly expected for use in a car air conditioner, a refrigerator and the like. In case of the refrigerator, it is required to have a good compatibility between lubricant and refrigerant, and further the lubricant itself is necessary to have an electric insulating property because the motor is substantially existent in the refrigeration system. However, the conventional compounds examined as a lubricant for HFC-134a refrigerant inclusive of PAG disclosed in US Patent No. 4,755,316 are remarkably poor in the electric insulating property as compared with the conventional refrigeration mineral oil and high in the hygroscopicity.

It is, therefore, an object of the invention to provide a refrigeration lubricant having an excellent compatibility with a new refrigerant such as HFC-134a or the like within a wide temperature range, a high electric insulating property and a low hygroscopicity.

At the present, a part of commercially available esters is used in systems using refrigerants R-12, R-22 and the like, but is incompatible with HFC-134a as a new refrigerant or is very narrow in the compatible range therewith. In this connection, the inventors have aimed at the fact that the ester has a high electric insulating property, a low hygroscopicity, a good lubricity and a high stability as compared with PAG and made various studies with respect to the molecule design of the ester showing a wide range of compatibility with HFC-134a, and found that only esters having a considerably restricted structure can be used in the HFC-134a refrigeration system, and as a result, the invention has been accomplished.

According to a first aspect of the invention, there is the provision of a lubricant for hydrofluorocarbon refrigerant such as HFC-134a and the like comprising as a main component an ester comprised of neopentyl glycol and at least one straight or branched-chain monovalent fatty acid having a carbon number of 3-18.

According to a s cond aspect of th invention, th re is th provision of a lubricant for hydrofluorocarbon refrig rant such as HFC-134a and th like comprising as a main component an ster comprised of at least on of penta rythritol, dipenta rythritol and tripenta rythritol repr sented by th following g n ral formula (I):

$$\mathrm{H{-}(OCH_2{-}\underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{\underset{|}{\overset{|}{C}}}}{-}CH_2)_n{-}OH} \qquad (\mathrm{I})$$

(in which n is 1, 2 or 3), and at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18.

According to a third aspect of the invention, there is the provision of a lubricant for hydrofluorocarbon refrigerant such as HFC-134a and the like comprising as a main component an ester comprised of a polyvalent alcohol represented by the following general formula (II):

$$\mathrm{R{-}\underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{\underset{|}{\overset{|}{C}}}}{-}CH_2OH} \qquad (\mathrm{II})$$

(in which R is an alkyl group having a carbon number of not more than 3), at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18, and not more than 25 mol% per total fatty acid of at least one polybasic acid having a carbon number of 4-36.

In a preferred embodiment of the invention, the hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane (HFC-134a).

The refrigeration lubricant for refrigerant HFC-134a and the like according to the first invention comprises an ester obtained by esterifying neopentyl glycol with at least one straight or branched-chain monovalent fatty acid having a carbon number of 3-18 as a main component.

In the first invention, the reason why the carbon number of the monovalent fatty acid is limited to 3-18 is due to the fact that when the carbon number is less than 3, the viscosity is too low, while when it exceeds 18, the resulting ester becomes cloudy or becomes very poor in the compatibility with the refrigerant HFC-134a and the like.

As the monovalent fatty acid, mention may be made of propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid, nonanoic acid, 3,5,5-trimethyl hexanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, palmitooleic acid, stearic acid, isostearic acid, oleic acid, and the like.

In the first invention, at least one of these monovalent fatty acids is properly mixed and esterified with neopentyl glycol to obtain an ester satisfying desirable physical properties required for various refrigerators.

In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the like, it is preferable to use a mixture of straight chain fatty acid having a carbon number of 3-11, preferably 5-10 and a branched-chain fatty acid having a carbon number of 3-14, preferably 7-9 as the monovalent fatty acid. In this case, the amount of the straight or branched-chain fatty acid used is preferable to be not less than 50 mol% per the total monovalent fatty acid used.

According to the invention, in order to give a proper viscosity to the resulting ester, at least one polybasic acid having a carbon number of 4-36 may be esterified with neopentyl glycol in an amount of not more than 80 mol% per total fatty acid. Among the polybasic acids, considering the more compatibility with the refrigerant HFC-134a and the like and the physical properties of the resulting ester, a polybasic acid having a carbon number of 4-10 is preferable.

Concretely, the polybasic acid includes succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, maleic acid, trimellitic acid and so on. Moreover, the polybasic acid having a carbon number of not more than 3 is a special product and is difficult to be cheaply available and is poor in the stability of the ester after the synthesis. While, when the carbon number xc eds 36, th compatibility of th resulting est r with HFC-134a and th lik is larg ly low red. In th inv ntion, the reason why the amount of the polybasic acid added is limited to not mor than 80 mol% per the total fatty acid is due to the fact that wh n it exceeds 80 mol%, the g lation may be caused and it is difficult to obtain d sirabl physical properties.

Th ester compounds according to th first inv ntion can be obtain d by the est rification r action

through dehydration reaction b twe n th sp cified polyvalent alcohol and th specified fatty acid as mentioned above, or the g neral st rification reaction through an acid anhydride, an acid chloride or th lik as a d rivativ of th fatty acid.

Since the ester according to the invention can be obtained by th above m thod, the remaining acid value and hydroxyl value are not particularly critical. However, when the acid value exceeds 3, there may be caused an unfavorable phenomenon that the metal soap is formed and precipitated by the reaction with a metal used inside the refrigerator, so that the acid value is preferable to be not more than 3. Furthermore, when the hydroxyl value exceeds 50, there may be caused an unfavorable phenomenon that the resulting ester becomes cloudy, so that the hydroxyl value is preferable to be not more than 50.

The lubricant for refrigerant HFC-134a and the like according to the second invention comprises an ester obtained by esterifying at least one of pentaerythritol, dipentaerythritol and tripentaerythritol represented by the aforementioned general formula (I) with at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18 as a main component.

In the condensate of pentaerythritol, the polymerization degree may be determined in accordance with the viscosity required in the resulting synthesized ester.

In the second invention, the carbon number of the monovalent fatty acid is limited to 2-18 because when it exceeds 18, the resulting ester becomes cloudy or becomes very poor in the compatibility with the refrigerant HFC-134a and the like.

As the monovalent fatty acid, mention may be made of acetic acid, propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid, nonanoic acid, 3,5,5-trimethyl hexanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, palmitooleic acid, stearic acid, isostearic acid, oleic acid, linoleic acid, linolenic acid and the like.

In the second invention, at least one of these monovalent fatty acids is properly mixed and esterified with pentaerythritol or its condensate to obtain an ester satisfying desirable physical properties required for various refrigerators.

In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the like, it is preferable to use a mixture of straight chain fatty acid having a carbon number of 3-11, preferably 5-10 and a branched-chain fatty acid having a carbon number of 3-14, preferably 7-9 as the monovalent fatty acid. In this case, the amount of the straight or branched-chain fatty acid used is preferable to be not less than 50 mol% per the total monovalent fatty acid used.

On the other hand, in order to give a proper viscosity to the resulting ester, at least one polybasic acid having a carbon number of 4-36 may be esterified with at least one of pentaerythritol, dipentaerythritol and tripentaerythritol in an amount of not more than 80 mol% per total fatty acid. In this case, the same polybasic acids as described in the first invention are used in the same manner as in the first invention.

The ester compounds according to the second invention can be obtained by the same method as in the first invention.

In the esters according to the second invention, the acid value is preferable to be not more than 3 and the hydroxyl value is preferable to be not more than 50 likewise the case of the first invention.

The lubricant for refrigerant HFC-134a and the like according to the third invention comprises an ester obtained by esterifying a polyvalent alcohol represented by the aforementioned general formula (II) with at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18 and not more than 25 mol% per total fatty acid of at least one polybasic acid having a carbon number of 4-36 as a main component.

When the carbon number of R in the general formula (II) is not less than 4, the compatibility of the resulting ester with HFC-134a and the like is largely lowered. As the polyvalent alcohol, mention may be made of trimethylol ethane, trimethylol propane, trimethylol butane and the like.

In the third invention, when the carbon number of the monovalent fatty acid is more than 18, it becomes very poor in the compatibility of the resulting synthesized ester with HFC-134a and the like. Particularly, the straight or branched-chain monovalent fatty acids having a carbon number of 3-10 are preferable. As the monovalent fatty acid, mention may be made of the same compounds as described in the second invention.

As to the polybasic acid, the polybasic acid having a carbon number of not more than 3 is a special product and is difficult to be cheaply available and is poor in the stability of the ester after the synthesis. While, when th carbon number xceeds 36, th compatibility of th r sulting est r with HFC-134a and th lik is larg ly low red. Th r for , the carbon number of the polybasic acid is pr ferabl to be 4-36, and particularly th carbon number of 4-10 is favorabl for nsuring th compatibility with HFC-134a at a wid range. As the polybasic acid, m ntion may be mad of adipic acid, az laic acid, sebacic acid and so on. Pr ferably, the monovalent fatty acid is 2-ethylh xanoic acid, and th polybasic acid is adipic acid.

Moreov r, th r ason why th amount of th polybasic acid added in th inv ntion is limit d to not more than 25 mol% per th total fatty acid is due to the fact that when it xceeds 25 mol%, the gelation may be caused and it is difficult to obtain desirabl physical properti s.

Th est r compounds according to th third inv ntion can be obtained by th same method as in th first and second inventions. In any case, it is desirable that the ester does not contain carboxyl group.

The esters according to the invention exhibit a good compatibility with the refrigerant HFC-134a and the like over a wide range of from low temperature to high temperature as a lubricant for use in a refrigerator using HFC-134a as a refrigerant, whereby the lubricity and thermal stability of the refrigeration lubricant can be considerably improved. Furthermore, they are high in the electric insulating property and small in the hygroscopicity as compared with PAG conventionally examined as a refrigeration lubricant for HFC-134a. Therefore, the refrigeration lubricants comprising the ester according to the invention as a main component can solve the problems on the compatibility with HFC-134a and the hygroscopicity, which have never been solved in the conventional technique, and can further enhance the electric insulating property, which comes into problem when HFC-134a is used in a compressor for a refrigerator.

Moreover, additives usually used in the lubricant such as antioxidant, anti-wear agent, epoxy compound and the like may properly be added to the refrigeration lubricant according to the invention.

The following examples are given in illustration of the invention and are not intended as limitations thereof.

Examples 1-8, Comparative Examples 1-5

The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to eight esters A-1 - A-8 shown in the following Table 1 (all of which esters were not commercially available but were prepared according to the first invention). For the comparison, the same evaluation as mentioned above was made with respect to commercially available PAG (B-1 - B-3, made by Asahi Denka Co., Ltd.) and esters (C-1 - C-2, made by Nippon Oil and Fats Co., Ltd.) as a refrigeration lubricant shown in the following Table 2.

The lubricity, compatibility, thermal stability, electric insulating property and hygroscopicity as performances of the refrigeration lubricant for the compressor shown in Tables 1 and 2 were evaluated under the following conditions.

Lubricity

Seizuring load (Falex load-carrying capacity) was measured according to ASTM D-3233-73 under a controlled atmosphere of HFC-134a blown.

Compatibility

After 0.6 g of the test lubricant and 2.4 g of the refrigerant (HFC-134a) were sealed in a glass tube, the cooling at 1°C/min and the heating were carried out, during which a temperature causing two-phase separation was measured.

Thermal stability

After 1 g of the test lubricant, 1 g of the refrigerant (HFC-134a or R-12) and a catalyst (wire of iron, copper or aluminum) were sealed in a glass tube, the mixture was heated to 175°C, and a color of the lubricant after 10 days was judged by ASTM color system according to ANSI/ASHRAE 97-1983.

Electric insulating property

It was evaluated by a dielectric constant at 80°C according to JIS C-2101.

Hygroscopicity

Into a beak r of 100 mℓ was charged 60 g of th test lubricant, which was l ft to stand at a t mperatur of 25°C and a humidity of 70% for 3 hours and then th water concentration was measured.

The valuation results ar shown in th following Tabl 3.

Table 1

Item / Ester	Straight chain fatty acid				Branched-chain fatty acid				Polybasic acid		Dynamic viscosity at 40°C (cSt)	Color (ASTM)
	C_5	C_8	C_{12}	C_{18}	C_7	C_8	C_9	C_{18}	adipic acid	sebacic acid		
A-1	30	20	-	-	-	50	-	-	-	-	4.6	L 0.5
A-2	30	-	10	10	50	-	-	-	-	-	7.0	L 0.5
A-3	10	-	-	10	40	-	40	-	-	-	14.4	L 0.5
A-4	-	20	-	-	75	-	-	5	-	-	6.5	L 0.5
A-5	-	5	10	-	-	75	-	-	10	-	11.9	L 0.5
A-6	-	10	-	-	65	-	-	-	-	25	20.9	L 0.5
A-7	-	-	-	-	-	100	-	-	-	-	7.4	L 0.5
A-8	-	10	-	-	40	-	10	-	40	-	22.1	L 0.5

Note) Amount of starting material was represented by mol%.

Table 2

	Type	Trade name	Color (ASTM)	Dynamic viscosity at 40°C (cSt)
B-1	PAG 1	Adekapol M-30 1)	L 0.5	32.8
B-2	PAG 1	Adekapol M-110 2)	L 0.5	105.2
B-3	PAG 1	Adekapol MH-50 3)	L 0.5	54.6
C-1	ester	dioctyl sebacate	L 0.5	11.4
C-2	ester	Unistar MB-816 4)	L 0.5	8.1

1) polyoxypropylene glycol monoalkyl ether
2) polyoxypropylene glycol monoalkyl ether
3) polyoxyethylene propylene glycol monoalkyl ether
4) monoester of 2-ethylhexanol and palmitic acid

Table 3

	Test lubricant	Dielectric constant at 80°C (Ω·cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
						refrigerant R-12		refrigerant HFC-134a		
			low temperature	high temperature		color (ASTM)	sludge	color (ASTM)	sludge	
Acceptable Example	A-1	7.5×10^{12}	≤-50 *	80≤ **	510	L 1.0	none	L 1.0	none	320
	A-2	6.1×10^{12}	≤-50	80≤	519	L 1.0	none	L 1.0	none	335
	A-3	4.9×10^{13}	≤-50	80≤	555	L 1.0	none	L 1.0	none	309
	A-4	1.7×10^{13}	≤-50	80≤	541	L 1.0	none	L 1.0	none	317
	A-5	8.0×10^{12}	-45	80≤	572	L 1.0	none	L 1.0	none	364
	A-6	5.6×10^{12}	-41	80≤	603	L 1.0	none	L 1.0	none	371
	A-7	2.6×10^{13}	≤-50	80≤	569	L 1.0	none	L 1.0	none	315
	A-8	4.8×10^{12}	-36	80≤	648	L 1.0	none	L 1.0	none	330
Comparative Example	B-1	2.1×10^{7}	≤-50	67	430	8.0≤	many	L 1.0	none	1600
	B-2	2.8×10^{7}	insoluble	insoluble	460	8.0≤	many	L 1.0	none	1200
	B-3	$\leq 10^{7}$	≤-50	53	430	8.0≤	many	L 1.0	none	2100
	C-1	5.1×10^{12}	insoluble	insoluble	570	L 1.0	none	L 1.0	none	340
	C-2	4.3×10^{12}	insoluble	insoluble	590	L 1.0	none	L 1.0	none	365

* : not higher than -50°C
** : not lower than 80°C

As seen from Table 3, when the esters according to the invention are compared with the conventional PGA (B-1 - B-3), th lectric insulating prop rty r pr sent d by th di lectric constant is 100,000 tim s or more and th two-phas separation at a high temperatur is not caused. Furthermor , the s izuring load is excellent and th hygroscopicity is low. Th thermal stability is equal in case of th HFC-134a system, but is consid rably xcell nt in case of th R-12 syst m. This is v ry advantageous in practical use because the mixing of HFC-134a and R-12 is not avoided at a stag of replacing the refrig rant from R-12 to HFC-

134a.

On th other hand, when the sters according to th inv ntion are compared with th commercially availabl sters (C-1 - C-2), th two-phas separation t mperatur is xtrem ly diff r nt and th conv n-tional esters are insoluble in HFC-134a. In this point, the molecul d sign d st rs according to th invention have a great merit.

As seen from the above, the esters according to the invention are fairly excellent in the performances as a lubricant as compared with Comparative Examples.

Examples 9-17

The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to nine esters A-9 - A-17 shown in the following Table 4 (all of which esters were not commercially available but were prepared according to the second invention). The same evaluation as in Example 1 was made to obtain results as shown in the following Table 5.

Table 4

Item / Ester	Polyvalent alcohol	Polybasic acid			Dynamic viscosity at 40°C (cSt)	Color (ASTM)
		straight chain fatty acid (mol%)	branched-chain fatty acid (mol%)	polybasic acid (mol%)		
A-9	pentaerythritol	——	isononanoic acid (100)	——	125.4	L 0.5
A-10	pentaerythritol	pentanoic acid (100)	——	——	14.5	L 0.5
A-11	pentaerythritol	propionic acid (70) stearic acid (30)	——	——	33.4	L 0.5
A-12	pentaerythritol	——	2-ethylhexanoic acid (100)	——	42.3	L 0.5
A-13	pentaerythritol	heptanoic acid (15)	isobutanoic acid (75)	adipic acid (10)	110.9	L 0.5
A-14	dipentaerythritol	propionic acid (30)	2-ethylhexanoic acid(70)	——	123.9	L 0.5
A-15	dipentaerythritol	isostearic acid (10)	isobutanoic acid (90)	——	68.4	L 0.5
A-16	dipentaerythritol	butanoic acid (95)	——	sebacic acid (5)	89.4	L 0.5
A-17	tripentaerythritol	propionic acid (20)	2-ethylhexanoic aid (80)	——	146.3	L 0.5

Note) Mol% is an amount per total acid.

Table 5

	Test lubricant	Dielectric constant at 80°C (Ω·cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
						refrigerant R-12		refrigerant HFC-134a		
			low temperature	high temperature		color (ASTM)	sludge	color (ASTM)	sludge	
Acceptable Example	A-9	6.5×10^{13}	-38	80≤	641	L 1.0	none	L 1.0	none	292
	A-10	1.2×10^{13}	≤-50	80≤	524	L 1.0	none	L 1.0	none	319
	A-11	7.6×10^{12}	≤-50	80≤	541	L 1.0	none	L 1.0	none	344
	A-12	1.7×10^{13}	≤-50	80≤	549	L 1.0	none	L 1.0	none	331
	A-13	4.1×10^{12}	-43	80≤	610	L 1.0	none	L 1.0	none	348
	A-14	2.6×10^{12}	-40	80≤	623	L 1.0	none	L 1.0	none	325
	A-15	1.4×10^{13}	≤-50	80≤	581	L 1.0	none	L 1.0	none	339
	A-16	5.1×10^{12}	≤-50	80≤	602	L 1.0	none	L 1.0	none	358
	A-17	4.5×10^{12}	-31	80≤	654	L 1.0	none	L 1.0	none	324

As seen from Table 5, when the esters according to the invention are compared with the conventional PGA (B-1 - B-3) shown in Tabl s 2 and 3, th electric insulating property r present d by th di l ctric constant is 100,000 times or mor and th two-phase separation at a high t mperatur is not caused. Furthermore, th seizuring load is excell nt and the hygroscopicity is low. The th rmal stability is equal in cas f th HFC-134a syst m, but is consid rably xcell nt in case of th R-12 system. This is v ry advantageous in practical us becaus the mixing of HFC-134a and R-12 is not avoided at a stag of

replacing the refrigerant from R-12 to HFC-134a.

On the oth r hand, wh n the esters according to th invention are compared with th comm rcially availabl st rs (C-1 - C-2) shown in Tables 2 and 3, th two-phas s paration temp rature is xtremely diff rent and th conv ntional est rs ar insoluble in HFC-134a. In this point, th molecul designed st rs according to the invention have a great merit.

As seen from the above, the esters according to the invention are fairly excellent in the performances as a lubricant as compared with Comparative Examples.

The HFC-134a has been mentioned as a possible replacement for R-12 and is used for car air conditioner, refrigerator and the like. Particularly, in case of the car air conditioner, the compressor is driven in summer season, so that the compatibility between oil and refrigerant at high temperature becomes important. When the two-phase separation between oil and refrigerant is caused in the compressor during the driving, the refrigerant having a larger specific gravity remains in the lower portion of the compressor, resulting in the occurrence of compressor seizuring.

In case of the refrigerator, the motor is included in the compressor, so that leakage of electricity comes into problem. In this connection, the esters according to the invention have a dielectric constant higher by 100,000 times or more than that of the conventional PAG and are excellent in the electric insulating property, so that they can be said to be a refrigeration lubricant for the refrigerator.

Concretely, lubricants having a dynamic viscosity of 10-50 cSt at 40 °C are used as a lubricant for the refrigerator requiring a two-phase separation temperature of not higher than -40 °C, so that the esters A-10, A-11 and A-12 are particularly suitable therefor. On the other hand, lubricants having a dynamic viscosity of 80-150 cSt at 40 °C are used as a lubricant for the car air conditioner requiring a two-phase separation temperature of not higher than -20 °C, so that the esters A-9, A-13, A-14, A-16 and A-17 are particularly suitable therefor.

Examples 18-25

The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to eight esters A-18 - A-25 shown in the following Table 6 (all of which esters were not commercially available but were prepared according to the third invention). The same evaluation as in Example 1 was made to obtain results as shown in the following Table 7.

Table 6

Item / Ester	Polyvalent alcohol	Monovalent fatty acid	Polybasic acid	Color (ASTM)	Dynamic viscosity at 40°C (cSt)
A-18	trimethylol ethane	2-ethylhexanoic acid (100)	—	L 0.5	17.9
A-19	trimethylol ethane	2-ethylhexanoic acid (95)	azelaic acid (5)	L 0.5	84.1
A-20	trimethylol ethane	2-ethylhexanoic acid (90)	sebacic acid (10)	L 0.5	105.4
A-21	trimethylol ethane	heptanoic acid (100)	—	L 0.5	15.1
A-22	trimethylol ethane	octanoic acid (50) isononanoic acid (50)	—	L 0.5	18.2
A-23	trimethylol ethane	nonanoic acid (70) isononanoic acid (30)	—	L 0.5	20.4
A-24	trimethylol propane	2-ethylhexanoic acid (100)	—	L 0.5	19.1
A-25	trimethylol propane	heptanoic acid (60) 2-ethylhexanoic acid (40)	—	L 0.5	15.4

Note) numerical value in parenthesis is mol% per total fatty acid

Table 7

	Test lubricant	Dielectric constant at 80°C (Ω·cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
						refrigerant R-12		refrigerant HFC-134a		
			low temperature	high temperature		color (ASTM)	sludge	color (ASTM)	sludge	
Acceptable Example	A-18	5.6×10^{12}	≤−50	80≤	564	L 1.0	none	L 1.0	none	324
	A-19	1.9×10^{12}	−30	80≤	612	L 1.0	none	L 1.0	none	368
	A-20	2.8×10^{12}	−28	80≤	641	L 1.0	none	L 1.0	none	359
	A-21	7.6×10^{12}	−41	80≤	541	L 1.0	none	L 1.0	none	317
	A-22	5.9×10^{12}	≤−50	80≤	550	L 1.0	none	L 1.0	none	326
	A-23	3.1×10^{13}	−38	80≤	581	L 1.0	none	L 1.0	none	333
	A-24	8.6×10^{12}	≤−50	80≤	534	L 1.0	none	L 1.0	none	319
	A-25	4.3×10^{12}	≤−50	80≤	519	L 1.0	none	L 1.0	none	321

As seen from Tabl 7, wh n th sters according to the inv ntion ar compared with th conv ntional PGA (B-1 - B-3) shown in Tabl s 2 and 3, th lectric insulating property r pr sented by th dielectric constant is 100,000 times or mor and th two-phas separation at a high t mperature is not caused. Furth rmor , th s izuring load is xcell nt and th hygroscopicity is low. Th th rmal stability is equal in case of th HFC-134a system, but is considerably excell nt in cas of the R-12 system.

R cently, HFC-134a causing substantially no br akag of ozon lay r is closed up instead of R-12 widely used as a refrig rant in order to cope with th breakag of ozon layer through chlorofluorocarbon and hydrochlorofluorocarbon being a gr atest problem in world-wid scal , but is poor in th compatibility with the conventional refrigeration lubricant, which is a bar for th d v lopm nt of r placement system. However, the refrigeration lubricants according to the invention have a sufficient compatibility with HFC-134a as a refrigerant and a high electric insulating property and also are excellent in the total performances, so that they have an effect that the conventional systems can be used as they are even when HFC-134a is used instead of the conventional R-12 and R-22 as a refrigerant.

Claims

1. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of trimethylol ethane, trimethylol propane and trimethylol butane with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18.

2. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of trimethylol ethane, trimethylol propane and trimethylol butane with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 3-18 and (c) at least one saturated polybasic acid having a carbon number of 4-10 in which an amount of said saturated polybasic acid is not more than 25 mol% per total of said monovalent saturated fatty acid and said saturated polybasic acid used.

3. The use according to claim 1 or claim 2, wherein said monovalent saturated fatty acid is a straight chain monovalent saturated fatty acid and/or a branched-chain monovalent saturated fatty acid having a carbon number of 3-10.

4. The use according to claim 3, wherein said monovalent saturated fatty acid is selected from the group consisting of pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, isoheptanoic acid, 2-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-ethylpentanoic acid, 3-ethylpentanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, isooctanoic acid, 2-methylheptanoic acid, 3-methylheptanoic acid, 4-methylheptanoic acid, 2-ethylhexanoic acid, 2-propylpentanoic acid, 2,2-dimethylhexanoic acid, 2,4-dimethylhexanoic acid, 3,5-dimethylhexanoic acid, 2,2,4-trimethylpentanoic acid, isononanoic acid, 2-methyloctanoic acid, 3-methyloctanoic acid, 2,2-dimethylheptanoic acid, 2-ethylheptanoic acid and 3,5,5-trimethylhexanoic acid.

5. The use according to anyone of claims 1 to 4, wherein said ester has a hydroxyl value of not more than 50, a dielectric constant at 80°C of not less than 10^{12} Ω • cm and a two-phase separation temperature at low temperature side of not higher than -25°C in the coexistence with said hydrofluorocarbon refrigerant.

6. The use according to anyone of claims 1 to 5, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.

7. The use according to claim 2, wherein said saturated polybasic acid is selected from the group consisting of succinic acid, glutaric acid, adipic acid, suberic acid, pimelic acid, azelaic acid and sebacic acid.

8. A lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of trimethylol ethane, trimethylol propane and trimethylol butane with (b) at least one straight chain or branched-chain monoval nt saturated fatty acid having a carbon number of 2-18.

9. A lubricant for compr ssors using a hydrofluorocarbon r frigerant containing no chlorine, comprising as a main compon nt an est r(s) obtained by reacting (a) at least on polyval nt alcohol selected from th group consisting of trim thylol than , trimethylol propane and trimethylol butan with (b) at least on

straight chain or branched-chain monoval nt saturated fatty acid having a carbon number of 3-18 and (c) at least one saturated polybasic acid having a carbon number of 4-10 in which an amount of said saturated polybasic acid is not mor than 25 mol% per total of said monoval nt saturated fatty acid and said saturat d polybasic acid used.